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13. ABSTRACT (Maximum 200 words) <p>The objective of this program is the synthesis and characterization of new families of optically responsive materials for use in optical device fabrication. The materials that have been developed are <i>polysilsesquioxanes</i>, hybrids of organic network polymers and inorganic oxides.</p> <p>The materials are prepared by sol-gel techniques employing <i>molecular building blocks</i> that contain a variable organic component and an inorganic oxide precursor. The resulting materials are <i>molecular composites</i> with no phase boundary between the organic and inorganic domains.</p> <p>Where the organic component of the molecular building block contains a chromophore with known NLO properties, optically responsive materials can be produced. In our efforts we have produced optical quality thin films by a combined sol-gel/electric field poling technique. The resulting poled thin films exhibit d33 and r33 figures of merit of 35-37 (pm/V) and 9-10 (pm/V). These values are comparable to that of lithium niobate. Work is continuing to enhance the d33 and r33 values as well as to improve the optical stability at elevated temperatures.</p> <p>In a relatively new effort we are developing methods for preparing optically transparent films and monoliths doped with quantum sized transition metal clusters. We have made an initial discovery that these materials have extremely high χ^3 coefficients.</p>					
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AFOSR Final Report
F49620-92-J-0379

Sol-Gel Approach to NLO Materials

Our research program is in the area of synthesis, fabrication and characterization of hybrid inorganic-organic materials. The materials, bridged polysilsesquioxanes, are prepared by sol-gel polymerization of molecular building blocks that contain both organic and inorganic components (Figure 1).

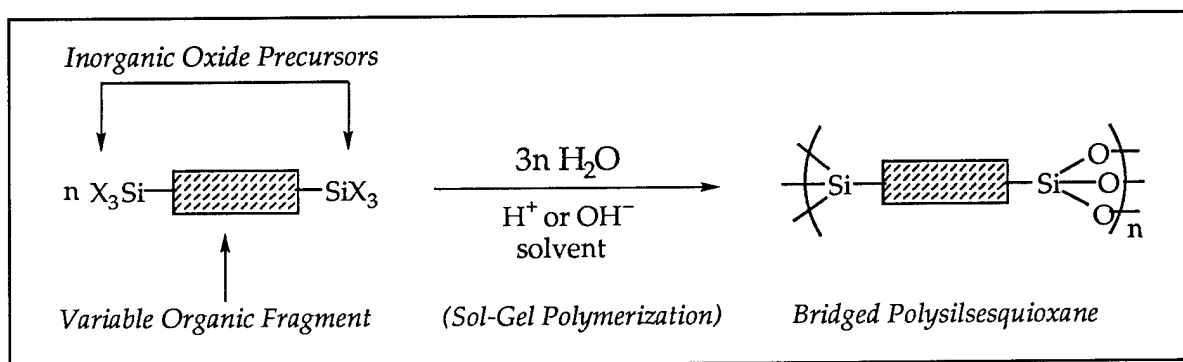


Figure 1. Schematic for the preparation of bridged polysilsesquioxanes by sol-gel polymerization.

These materials may be viewed *molecular composites* of an inorganic oxide and an organic fragment. The sol-gel polymerization conditions are quite mild and are compatible with a wide range of organic functionality. Typically, the polymerizations consist of alcohol or ether solutions of the molecular building block, together with catalyst and water. The solutions can be cast as tough, optically transparent thin films, drawn as fibers, or, following gelation, air dried to produce a condensed *xerogel* or supercritically processed to yield an *aerogel*. Their processability parallels that of sol-gels of pure silica.

We have been exploring sol-gel polymerization of molecular building blocks for fabrication of NLO materials. We employ two approaches to this problem. For X^2 materials, the NLO responsive chromophore is incorporated into the molecular building block and optically transparent films are produced by spin casting. For X^3 materials, optically transparent films containing quantum-sized metal clusters are produced. Both techniques give rise to materials with high nonlinearities.

X² Materials

For X² materials, sol-gel processable molecular building blocks incorporating organic fragments with known NLO chromophores are prepared. Representative sol-gel processable monomers are shown in Figure 2. We have developed procedures for simultaneous sol-gel polymerization/spin casting/poling and curing of these monomers. A typical polymerization formulation consists of monomers in an organic solvent. The catalyst for sol-gel polymerization is added and film is spun-cast. The samples are simultaneously polled and cured as the evolution of the NLO signal is monitored. Optical-quality films with substantial nonlinearities can be produced by this approach (Table 1).

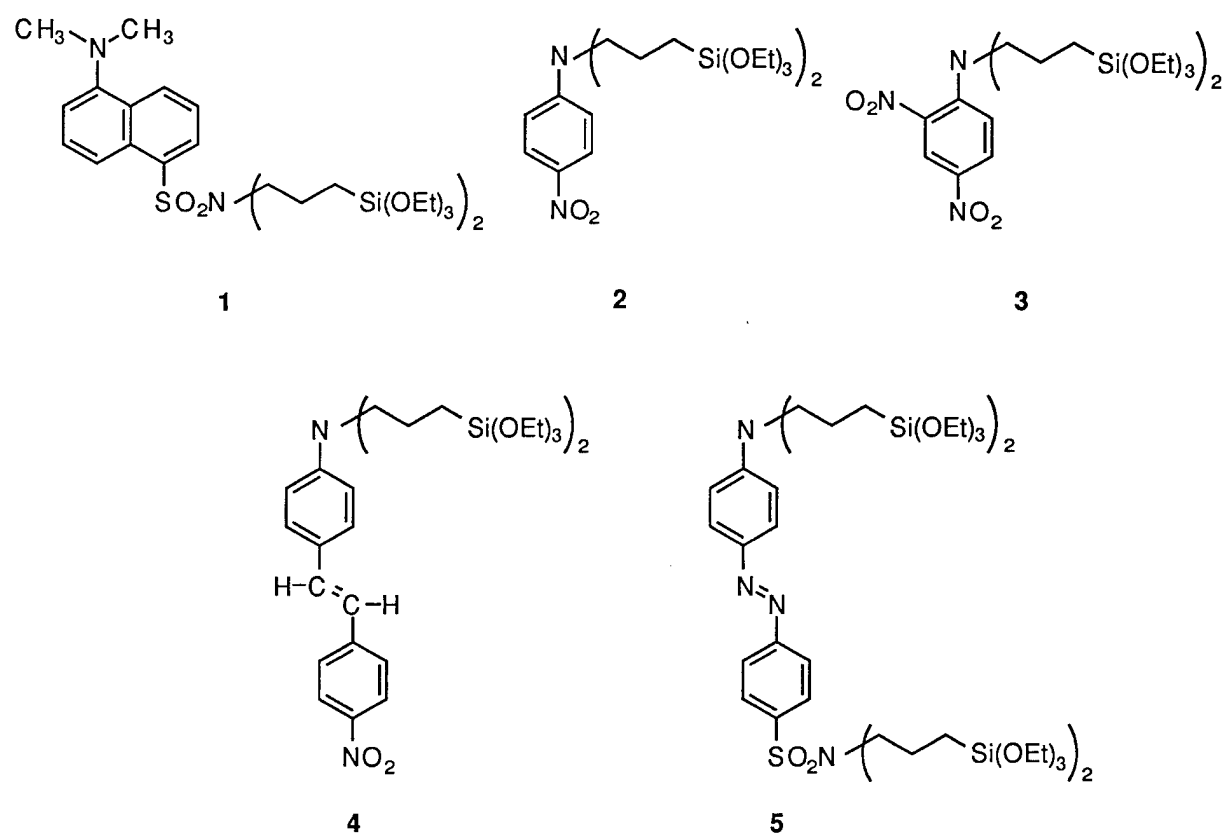
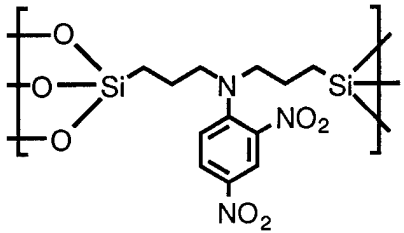
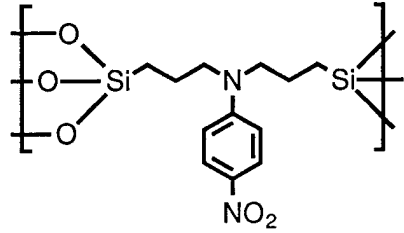


Figure 2.

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Table 1. d_{33} and r_{33} Coefficients of Poled Sol-gel Films

	d_{33} (pm /V)	r_{33} (pm/V)
	9-10	2-2.5
	35-37	9-10
Lithium Niobate LiNbO_3 (bulk)	44	29

There are a number of advantages to the sol-gel approach:

- (1) The covalent attachment of the organic and inorganic elements ensures no phase separation between the matrix and NLO material.
- (2) High loadings can be prepared since every monomer contains a chromophore. Over 50% by weight of chromophore is readily achieved.
- (3) Mild processability. The initial stages of sol-gel polymerization are performed at room temperature while poling and curing requires temperatures of only 150 °C. These are well below the decomposition temperature of the material.
- (4) Optical quality films and monoliths are readily prepared.
- (5) The process is amenable to incorporating a very wide range of organic chromophores.

An important problem that must be resolved for successful device fabrication is the maintenance of the *orientational stability* of the molecular dipoles at elevated temperatures. The use of sol-gel NLO systems for second order applications requires electric field poling to destroy the isotropic molecular symmetry of the chromophore ensemble.

In our first study, thin films from monomer **2** were spincoated onto indium tin oxide (ITO) coated glass slides and heated to 180 °C in air at a rate of 10 °C/min. The film was held at 180 °C for approximately 30 min during poling then cooled to room temperature.

The d_{33} values of poled, cured films from monomer **2** were indefinitely stable at room temperature. However, the d_{33} value falls off rapidly at temperatures above 100 °C (Figure 3). When the cured film is heated to 150 °C, the d_{33} value could be restored by repoling, suggesting that the decay of X^2 at elevated temperatures arises from the mobility of the chromophore in the matrix and *not* from decomposition. Our efforts directed at achieving orientational stability in these sol-gel films at elevated temperatures have been fruitful.

In a study performed by Jarek Zieba in Professor Prasad's group at SUNY Buffalo, the poling time was increased to 4 hours at 180 °C under a *dry nitrogen* atmosphere. The resultant materials showed a dramatic increase in the thermal stability of the SHG signal (Figure 4). Apparently, this extended curing time under the different condition utilized "locked" the orientation of the dipoles into place in the organic/inorganic polysilsesquioxane. Thus, the SHG signal is stable at 150 °C for over 1 hour and even at 175 °C, approximately 60% of the SHG signal is present after 4 hours. Additional studies have been performed with materials prepared from **2** and have demonstrated the reproducibility.



Figure 3.

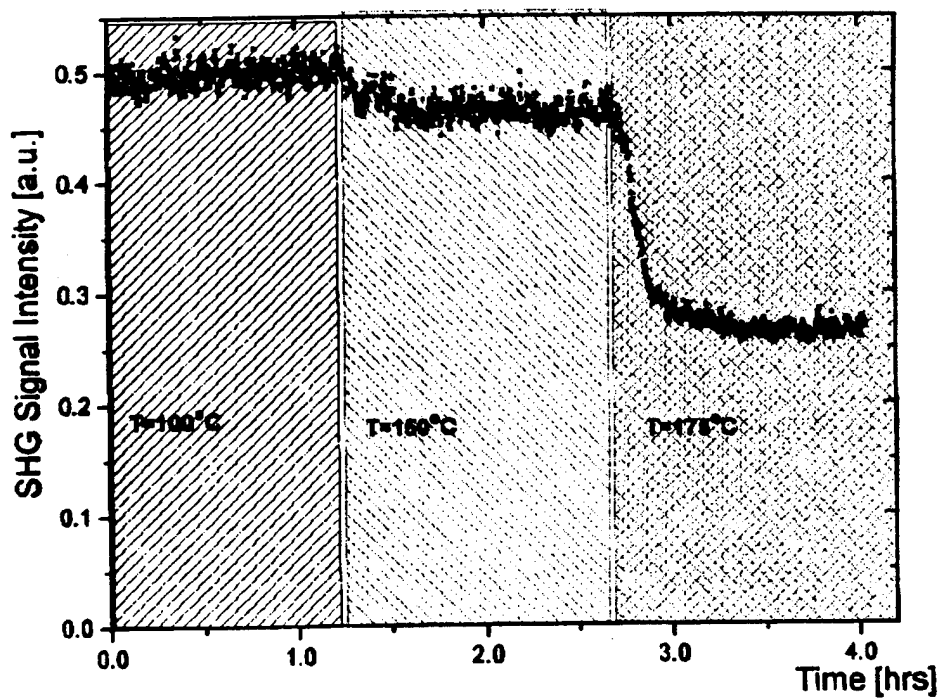


Figure 4.

X³ Materials

A second area of research is the fabrication of novel X³ responsive materials. One of our approaches is to produce sol-gel processable optical quality films and monoliths that are doped with quantum-sized transition metal clusters. We are currently able to produce thick glass films of high optical quality containing Cr metal clusters and "CrO" phases by the procedure outlined in Figure 5. A metal precursor (a π -arene complex) is incorporated into the sol-gel polymerization reaction. Following sol-gel polymerization and drying, the clear film is heated to 125 °C in vacuum to liberate carbon monoxide and deposit chromium metal. The resulting material contains microcrystalline chromium clusters that range in size from 20 to 90 Å.

The method is amenable to a number of sol-gel processable transition metal containing monomers (Figure 6). Our preliminary qualitative investigation of the Cr/"CrO" doped film shows a substantial X³ response (X5 CS₂). The potential benefits of these materials are:

- (1) A mild sol-gel method for producing novel optical quality films, fibers, and monoliths with a high X³ response.
- (2) Unlike highly conjugated organic polymers, which require chemical doping, the sol-gel process does not require any subsequent chemical deposition or transformation to produce the X³ active species.
- (3) The metal-containing films are stable and do not require protection from the environment.
- (4) The process is amenable to the introduction of a wide range of metals and semiconductors.

The issues that need to be resolved are:

- (1) Quantification of the magnitude of the X³ response and evaluation of the response time.
- (2) Evaluation of the temporal stability and thermal stability of the X³ response.
- (3) Selection of the optimum metal/semiconductor phase for the desired application.

Summary

Sol-gel chemistry has been developed for the production of hybrid organic-inorganic materials with good optical properties and substantial X² and X³ responses. The mild processing and fabrication conditions makes these materials suitable for device fabrication.

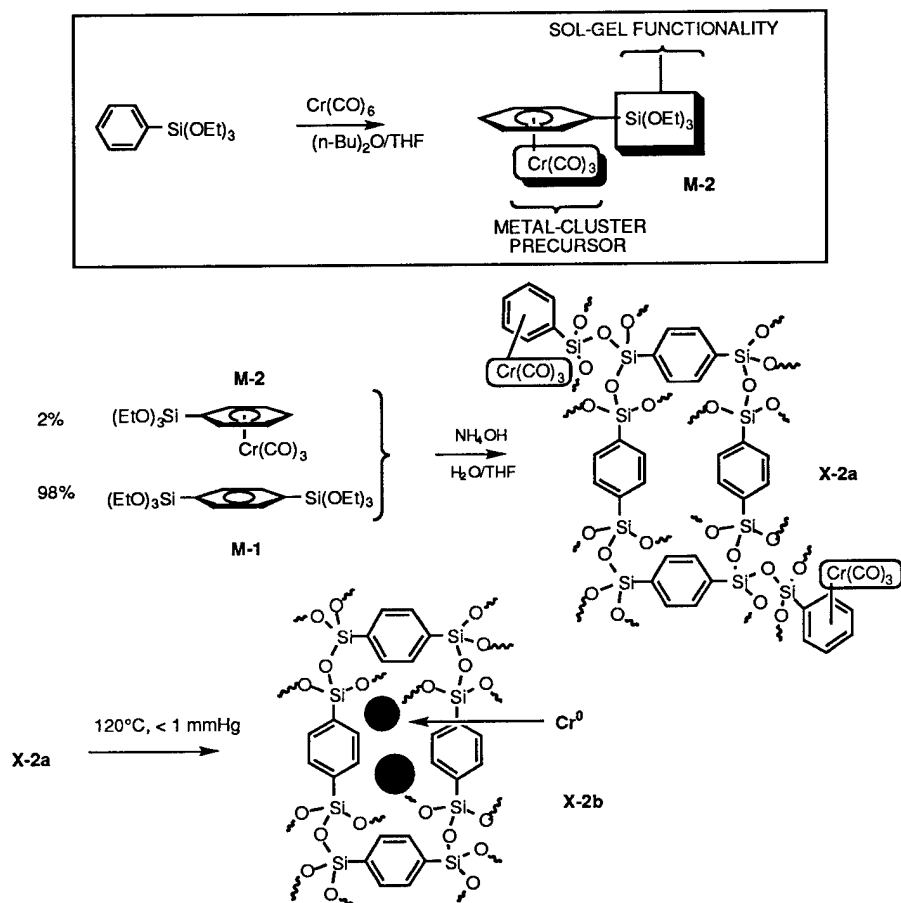


Figure 5.

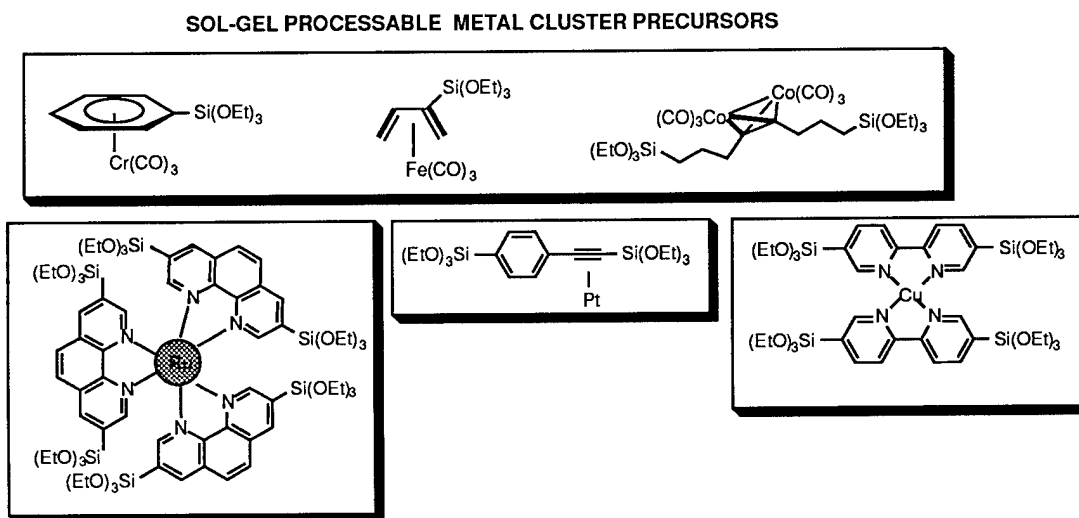


Figure 6.

Students Who Have Been Suported By AFOSR F49620-92-J-0379

Henry Oviatt - Graduate Student (Ph.D. 1994) - Dissertation Abstract

James Small - Graduate Student (Ph.D. 1995) - Dissertation Abstract

Stephen Hobson - Graduate Student

Joseph Tran - Graduate Student

Kyung M. Choi - Postdoctoral

Sean McHugh - Undergraduate Student

Publications Resulting from AFOSR F49620-92-J-0379

1. "Condensed Aryl-Bridged Siliconates. New Ladder and Network Ionomers," K. J. Shea, J. H. Small, and D. A. Loy, *Chemistry of Materials* **1992**, *4*, 255.
2. "Arylsilsesquioxane Gels and Related Materials. New Hybrids of Organic and Inorganic Networks," K. J. Shea, D. A. Loy and O. Webster, *J. Am. Chem. Soc.* **1992**, *114*, 6700.
3. "Hypervalent Siliconate Materials. Synthesis and Characterization of Novel Ladder and Network Ionomers," K. J. Shea, D. A. Loy and J. H. Small. "Better Ceramics Through Chemistry V, MRS Symposium Proceedings," **1992**, 271, 711.
4. "Preparation of Aryl-Bridged Polysilsesquioxane Aerogels," D. A. Loy, K. J. Shea, and E. M. Russic, "Better Ceramics Through Chemistry V, MRS Symposium Proceedings," **1992**, 271, 699.
5. "Arylene- and Alkylene-Bridged Siliconates," D. A. Loy, J. H. Small, and K. J. Shea, *Organometallics*, **1993**, *12*, 1484.
6. "Arylene-Bridged and Alkylene-Bridged Polysilsesquioxanes," D. A. Loy, K. J. Shea, and J. H. Small. *Journal of Non-Crystalline Solids*, **1993**, *160*, 234.
7. "Alkylene-Bridged Silsesquioxane Sol-Gel Synthesis and Xerogel Characterization. Molecular Requirements for Porosity," H. W. Oviatt, Jr., K. J. Shea, and J. H. Small, *Chemistry of Materials*, **1993**, *5*, 943.
8. "Porous Materials by Design. Plasma Oxidation of Hydrocarbon Templates in Polysesquioxanes," D. A. Loy, R. J. Buss, R. A. Assink, K. J. Shea, and H. W. Oviatt. *American Chemical Society Division of Polymer Chemistry, Polymer Preprints*, **1993**, *34*, 244.
9. "Bridged Polygermsesquioxanes. Organically Modified Germanium Oxide Materials," G. M. Jamison, D. A. Loy and K. J. Shea. *Chemistry of Materials*, **1993**, *5*, 1193.
10. "New Materials for Synthesis of Quantum-Sized Semiconductors and Transition-Metal Particles. Microporous Polysilsesquioxanes as a Confinement Matrix for Particle Growth," K. M. Choi and K. J. Shea. *Chemistry of Materials*, **1993**, *5*, 1067.

11. "Amorphous Polysilsesquioxanes as a Confinement Matrix for Quantum-Sized Particle Growth. Size Analysis and Quantum Size Effect of CdS Particles Grown in Porous Polysilsesquioxanes," K. M. Choi and K. J. Shea. *J. Phys. Chem.*, **1994**, *98*, 3207.
12. "Preparation and Characterization of Ultra-Small Sized Metal and Semiconductor Particles in Sol-Gel Materials," K. M. Choi and K. J. Shea, *Better Ceramics Through Chemistry VI, MRS Symposium Proceedings*, **1994**, 346, 763.
13. "Engineering of Porosity in Amorphous Materials. Plasma Oxidation of Hydrocarbon Templates in Polysilsesquioxanes," D. A. Loy, R. J. Buss, R. A. Assink, K. J. Shea and H. Oviatt, *Better Ceramics Through Chemistry VI, MRS Symposium Proceedings*, **1994**, 346.
14. "Preparation of Nano-Sized Chromium Clusters and Intimate Mixtures of Chromium/CdS Phases in a Porous Hybrid Xerogel by an Internal Doping Method," K. M. Choi and K. J. Shea, *J. Am. Chem. Soc.*, **1994**, *116*, 9052.
15. "Plasma Oxidation of Hydrocarbon Templates in Bridged Polysilsesquioxanes. Porous Materials by Design," D. A. Loy, K. J. Shea, R. J. Buss, and R. A. Assink, *Inorganic and Organometallic Polymers II*, P. Wisian-Neilson, H. R. Allcock, K. J. Wynn, Eds; *ACS Symposium Series*, **1994**, 572, 122.
16. "Hypervalent Spiro- Polysiliconate and Polygermylate Ionomers: Novel Ladder and Network Materials," J. H. Small. K. J. Shea, D. A. Loy and G. M. Jamison, *ACS Symposium Series 585: Hybrid Organic-Inorganic Composites*, **1995**, 248.
17. "Hexylene- and Phenylene-Bridged Polysilsesquioxane Network Materials," D. A. Loy, G. M. Jamison, R. A. Assink, S. A. Myers, K. J. Shea, , *ACS Symposium Series 585: Hybrid Organic-Inorganic Composites*, **1995**, 264.
18. "Organic Bridged Polysilsesquioxane Xerogels. Application to Non-Linear Optical Materials," H. W. Oviatt, Jr., K. J. Shea, S. Kallori, Y. Shi, W. H. Steier and L. R. Dalton, *Chemistry of Materials*, **1995**, *7*, 493.
19. "New Procedures for the Preparation of CdS and Heterogeneous Cr/CdS Phases in Hybrid Xerogel Matrices. Pore Structure Analysis and Characterization," K. M. Choi, J. C. Hemminger and K. J. Shea, *J. Phys. Chem.*, **1995**, *99*, 4720.